Angular dependence of NMR spectra of cholesteric liquid crystals

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The angular dependence of the second moment of the NMR lines of the protons of a cholesteric liquid crystal is investigated theoretically and experimentally. The possibilities of using NMR for the study of the structure of the cholesteric mesophase is considered.

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NMR is presently used extensively for the study of the structure of liquid crystals (LC) and is one of the most exact methods of determining the order parameter.[1] Its use is based on the fact that in LC, owing to the orientation ordering of the molecules, the dipole–dipole interaction of the nuclear magnetic moment does not average out to zero, and makes the principal contribution to the resonance line shape.

In the case of an oriented nematic LC, when all the molecules of the system are ordered about a single common direction—the director—the NMR spectrum is a doublet. An investigation of the distances between its lines makes it possible to calculate the components of the order-parameter tensor.[1–3]

In cholesteric liquid crystals (CLC) the NMR spectrum is a superposition of the spectra of individual nematic planes, turned relative to one another about the axis of the cholesteric helix. In addition, the molecules of substances that make up the CLC also contain a large number of interacting nuclei and have a rather complicated form. These factors lead to a smearing of the NMR lines of CLC and complicate the extraction of quantitative information from the NMR spectrum. Therefore, despite the large advantages of this method in the study of the LC structure, there are at present only two papers on the NMR of CLC.[4,5] Studies were made of only mixtures of cholesteric and nematic components, for which the threshold magnetic field intensity of the CLC–NCL transition is small ($H_c \sim 4000$ G) and it is possible to compare the NMR spectra of the cholesteric and nematic phases. It was shown[5] that for this class of substances a study of the dependence of the second moment of the NMR lines on the magnetic field intensity (H) makes it possible to obtain the value of the order parameter and to investigate the influence of H on the structure of the CLC.

We consider in this paper the opposite case of pure CLC, which have large values of H_c and whose structure changes little in the region of the resonant values of the magnetic field intensity. To extract quantitative information from the NMR spectra of these CLC we propose to use the angular dependence of the second moment of the resonance lines.

Assuming that the time of motion of the molecules about the local direction of the director is much shorter than the spin-lattice relaxation times of the nuclei and that the interaction of the nuclear spins averages out to zero as a result of this motion, we obtain from the general theory[6] the following expression for the second moment of the NMR lines:

$$M_2=\hbar^2\sum_{ij}\eta_{ij}\gamma_i\gamma_j I_j(I_j+1)r_{ij}^{-6}\langle\langle P_2(\cos\theta_{ij})\rangle_t^2\rangle_c, \tag{1}$$

in which the summation is over the nuclei of one molecule; γ_j and I_j are respectively the gyromagnetic ratio and the spin of the j-th nucleus; r_{ij} is the distance between the nuclei i and j; θ_{ij} is the angle between $\mathbf{r}_{ij}$ and $\mathbf{H}$; $P_2(\cos\theta_{ij})$ is a Legendre polynomial; $\eta_{ij}=3$ if the nuclei i and j are of the same sort and $\eta_{ij}=4/3$ in the opposite case; $\langle\cdots\rangle_t$ stands for time averaging of the orientation of $\mathbf{r}_{ij}$ with allowance for the rapid motion of the molecules around the director; $\langle\cdots\rangle_c$ is the configuration averaging, which takes into account the distribution of the local directions of the director n about the local directions of the axis of the cholesteric spiral $\mathbf{h}$ and the distribution of $\mathbf{h}$ in a coordinate system connected with the cell in which the CLC is located (Fig. 1).

Assuming that $\mathbf{n}\perp\mathbf{h}$ at all points of the system, that the order-parameter tensor components do not depend on the coordinates of the molecule, and that the motion of the molecules around n and the distribution of $\mathbf{n}$ around $\mathbf{h}$ and of $\mathbf{h}$ around the Z axis of the coordinate

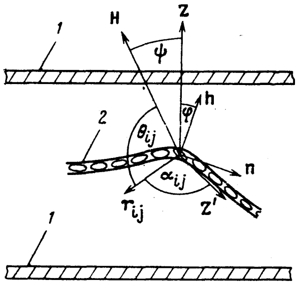

FIG. 1. Configuration of the axes around which the averagings are carried out in the calculation of the second moment of the NMR lines: 1—walls of cell in which the CLC is placed; 2—deformed nematic planes; Z′—"long" axis of the CLC molecule; Z—normal to the surface of the cell; h—local direction of the axis of the cholesteric helix; n—local direction of the director; $\mathbf{r}_{ij}$—interspin-distance vector.

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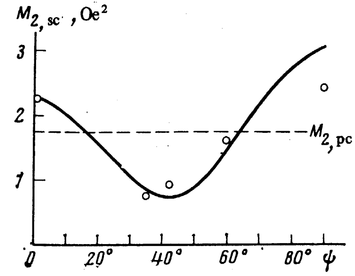

FIG. 2. Theoretical (solid curve) and experimental (points) dependences of the second moments of the NMR lines of oriented CLC liquids as functions of the direction of the magnetic field (see the text, case 2). M_{2pc} is the value of the second moment for a "polycrystal" (case 1).

system connected with the cell are characterized by cylindrical symmetry, we obtain

$$M_2(\psi)=5M_{2\,pc}\sum_{L,M=-2}^{2}[d_{OL}{}^2(\psi)]^2\langle[d_{LM}{}^2(\varphi)]^2\rangle_c\left[d_{MO}{}^2\left(\frac{\pi}{2}\right)\right]^2, \tag{2}$$

where d^2_{LM} is the modulus of the Wigner function,[7] ψ is the angle between **H** and **Z**, φ is the angle between **h** and **Z**, we get

$$M_{2\,pc}=\frac{\hbar^2}{20}\sum_{ij}\eta_{ij}\gamma_i\gamma_j I_j(I_j+1)r_{ij}{}^{-6}$$
$$\times[S_{Z'Z'}(3\cos^2\beta_{ij}-1)-(S_{X'X'}-S_{Y'Y'})\sin^2\beta_{ij}\cos 2\alpha_{ij}]. \tag{3}$$

Here β_{ij} and α_{ij} are the polar and azimuthal angles of the vector $\mathbf{r}_{ij}$ in the proper coordinate system of the order parameter $S_{\alpha\beta}(\alpha, \beta = X', Y', Z')$, the axes of which are rigidly connected with the molecules.[1,5]

As seen from formula (2) and (3), after performing the averaging, the second moment takes the form of a product of two factors, the first of which (M_{2pc}) contains information on the structure of the molecule and on the order-parameter tensor. The second describes the dependence of $M_2(\psi)$ on the orientation of the magnetic field relative to the cell and on the distribution of the local direction **h**.

Let us examine a number of particular cases of practical significance.

1. The orientation of the local axes **h** is random, i.e., the CLC is a "polycrystal" made up of randomly oriented "signal crystals." In this case

$$M_2(\psi)=M_{2\,pc}. \tag{4}$$

Measurements of M_{2pc} is convenient from the experimental point of view, since it does not require a prior orientation of the CLC. From the value of M_{2pc} we can determine the order parameter. Since usually $|S_{Z'Z'}| \gg |S_{X'X'} - S_{Y'Y'}|$, it follows that

$$M_{2\,pc}=AS^2, \tag{5}$$

where A is a constant that depends on the geometrical characteristics of the molecule $(r_{ij}, \alpha_{ij}, \beta_{ij})$, and $S=\frac{3}{2}S_{Z'Z'}=\langle P_2(\cos\widehat{\mathbf{Z}'\mathbf{n}})\rangle$ is the order parameter. With the aid of expressions (3)–(5) we can investigate the temperature dependence of the relative values of S. If the parameters of the molecule are known we can calculate also the absolute value of the order parameter.

2. The CLC consists of identically oriented nematic planes with $\mathbf{h} \parallel \mathbf{Z}$ ("single crystal"):

$$M_{2\,sc}(\psi)={}^5/_4M_{2\,pc}({}^{27}/_8\sin^4\psi-3\sin^2\psi+1). \tag{6}$$

3. The CLC has a texture close to planar

$$M_2(\psi)=M_{2\,sc}(\psi)-{}^5/_4M_{2\,pc}\langle\varphi^2\rangle_c({}^{81}/_8\sin^4\psi-12\sin^2\psi+1). \tag{7}$$

The quantity $\langle\varphi^2\rangle_c$ in (7) is the mean squared angle between **h** and **Z**. It can serve as an objective characteristic of the quality of the CLC orientation. On the other hand, $\langle\varphi^2\rangle_c$ can be calculated for a given type of perturbation of the planar texture and, by comparing the experimental value of $\langle\varphi^2\rangle_c$ with the calculated one, we can investigate the nature of the perturbation. For example, for a spatially-periodic perturbation produced by an electric field directed parallel to **h**,[8] we can obtain the expression

$$\langle\varphi^2\rangle_c=\frac{\pi^2}{4}\frac{K_2}{K_3}\frac{u_0{}^2}{PL} \tag{8}$$

in which K_2 and K_3 are the Frank elastic moduli, P is the pitch of the cholesteric helix, L is the distance between the oriented surfaces (the cell thickness), and u_0 is the amplitude of the displacements of the nematic planes. Thus, it becomes possible to use NMR to investigate the character of the electrodynamic instabilities in CLC.

To verify the assumptions made in the derivation of formulas (2) and (5)–(7), we investigated experimentally the angular dependence of $M_2(\psi)$ in the case of an oriented CLC and the value of M_{2pc} for the case of a "polycrystalline" sample. We investigated the composition with 30% cholesteryl chloride and 70% cholesteryl oleate. The measurements were performed with the RYa-2301 installation at room temperature. Proton resonance at a frequency 14 MHz was observed. The sample was oriented by placing the CLC between specially finished cover glasses gathered into a stack. The thickness of an individual layer was $L = 10\ \mu$m. The quality of the orientation was monitored by optical methods. The magnetic field used in the experiment ($H \approx 3000$ G) had no influence on the structure of the sample. The results of the measurements of the angular dependence of $M_2(\psi)$ are shown in Fig. 2. It is seen that the experimental $M_2(\psi)$ agrees satisfactorily with the theoretical dependence calculated from formula (6). The experimental ratio of $M_2(0)$ and M_{2pc} is also close to the calculated value – $\frac{5}{4}$ which follows from formulas (5) and (6).

The foregoing calculations and measurements demonstrate that the NMR method is highly promising for the investigation of CLC.

[1]M. J. Stephen and J. P. Straley, Rev. Mod. Phys. **46**, 617 (1974).
[2]A. Saupe and G. Englert, Phys. Rev. Lett. **11**, 462 (1963).
[3]A. Losche, Z. Phys. Chem. (Leipzig) **255**, 1157 (1974).
[4]R. J. Dong, M. M. Pintar, and W. Forbes, J. Chem. Phys. **55**, 2449 (1971).
[5]P. J. Collings, S. J. Goss, and J. R. McColl, Phys. Rev. **A11**, 682 (1975).
[6]C. P. Slichter, Principles of Magnetic Resonance, Harper & Row, 1963 (Russ. transl. Mir, 1967).
[7]D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskiĭ, Kvantovaya teoriya uglovogo momenta (Quantum Theory of Angular Momentum), Nauka, 1975.
[8]W. Helfrich, J. Chem. Phys. **55**, 839 (1971).

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Character of phase transitions to a helical or sinusoidal state in magnetic materials

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It is emphasized that the character of the transition from the paramagnetic state to a sinusoidal or spiral state depends significantly on the form of the magnetic interactions. Thus if there are only exchange interactions, of if they significantly exceed the spin-orbit or dipole-dipole forces, then only a first-order transition is possible. A transition of the second-order is possible only for a definite finite intensity of the relativisitic interactions. In this latter case, there are two tricritical points on the phase diagram.

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1. INTRODUCTION

Phase transitions in magnetic materials, especially transitions from the paramagnetic to the ferro- or antiferromagnetic state, are excellent examples of transitions of second order. But a large number of cases are now known in which magnetic phase transitions that, according to the symmetry considerations characteristic of Landau's theory (see, for example, Ref. 1), could be transitions of second order are actually found to be transitions of first order. A large number of examples of this can be found in the review by Grazhdankina.[2] New facts not mentioned in this review are reported in the articles[3–6] cited below. Until recently, such first-order transitions were explained within the framework of molecular-field theory, by the action of specific forces of rather large (in comparison with ordinary exchange) intensity: magnetostriction, biquadratic exchange, the Jahn-Teller effect, etc. (for details, see Ref. 2). Recently, however, it has been clarified that fluctuations of the short-range order, which increase with approach to a point of (in principle possible) second-order transition, act in the same direction as the just mentioned magnetostriction, biquadratic exchange, etc., tending to convert the continuous transition to a discontinuous one. Furthermore, it has been shown in papers of Brazovskiĭ, Kukharenko, and the author,[3,4] of Bak, Krinsky, and Mukamel,[5] and of Alessandrini, Cracknell, and Przystawa[6] that in certain cases the fluctuations make second-order transitions altogether impossible; that is, the transition is discontinuous even for arbitrarily weak interactions of the biquadratic-exchange type. Transitions of this form include those in MnO, UO_2, TbAs, etc.

From the point of view of molecular-field theory, what causes the transition to become discontinuous is a sufficiently strong nonlinear coupling between the effective field H_{eff} and the order parameter M:

$$H_{eff}=JM+jM^3+\ldots$$

For weak nonlinearity, $j \ll J$, the variation of M with temperature T is described by the usual Langevin-Brillouin curve (Curve 1 in Fig. 1). For sufficiently large j, M as a function of T ceases to be single-valued (Curve 3 in Fig. 1); this obviously implies a transition of the first order at some temperature T_0. From a physical point of view, the nonlinearity j originates from the already mentioned biquadratic exchange, magnetostriction, etc. A characteristic feature of such first-order transitions is the presence of a tricritical point T_{c0}, at which a line of first-order transitions is converted to a line of second-order transitions.

The effect of fluctuations on the character of the transition is as follows. In all cases analyzed, the magnetic phase that originates as a result of the transition is characterized by the presence of a large number of equivalent domains. This, for example, is 8 so-called T-domains in MnO, TbAs, etc. (see Refs. 3–5) or 6 domains in UO_2 (see Refs. 3–6). On approaching the transition point from above, the system of course cannot "know" into just which one of the 8 or 6 domains (or